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Recycling of rare earths from lamp phosphor waste: enhanced dissolution of $LaPO_4:Ce^{3+},Tb^{3+}$ by mechanical activation

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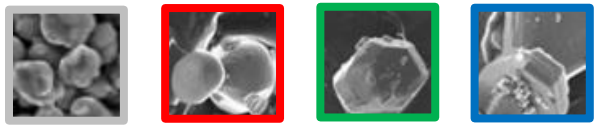
Recovery of critical (RE) metals

- High collection rate
- By 2020; around 25 000 tons of rare earths stockpiled
- Trichromatic phosphor blend + white-emitting phosphor
- Most critical REEs; Y, Eu and Tb

Type phosphor	Name	Content (wt%)[a]	Economic value
White	$Ca_{4.86}Mn_{0.10}Sb_{0.04}Sr_{0.004}(PO_4)_3Cl_{0.10}F_{0.90}$ (HALO)	40–50	Low
Red	$Y_2O_3:Eu^{3+}$ (YOX)	20	High
Green	$LaPO_4:Ce^{3+},Tb^{3+}$ (LAP)	6–7	High
	$CeMgAl_{11}O_{19}:Tb^{3+}$ (CAT)	6–7	High
Blue	$BaMgAl_{10}O_{17}:Eu^{2+}$ (BAM)	5	Low

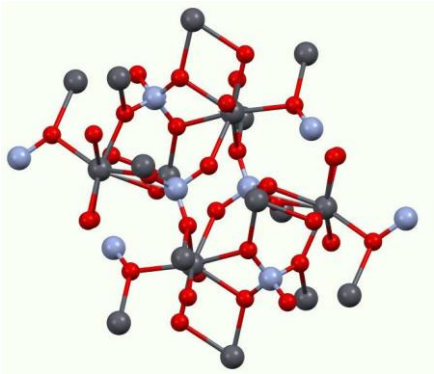
[a] Besides the presence of phosphors, the lamp waste consists of fine glass particles (up to 20 wt%), and Al_2O_3.

Recovery of critical (RE) metals



HALO YOX LAP CAT BAM

Unleachable in dilute mineral acids



Monazite

- LAP/CAT/BAM = refractory phosphor
- Leached using high acid concentrations (18 M H_2SO_4, 120-230 °C) or cracked with molten salts (NaOH or Na_2CO_3)
- Need for alternative pre-treatment prior to leaching

S. Kipp, V. Šepelák, K. D.Becker, Chemie in unserer Zeit, 2005, 39, 384-394

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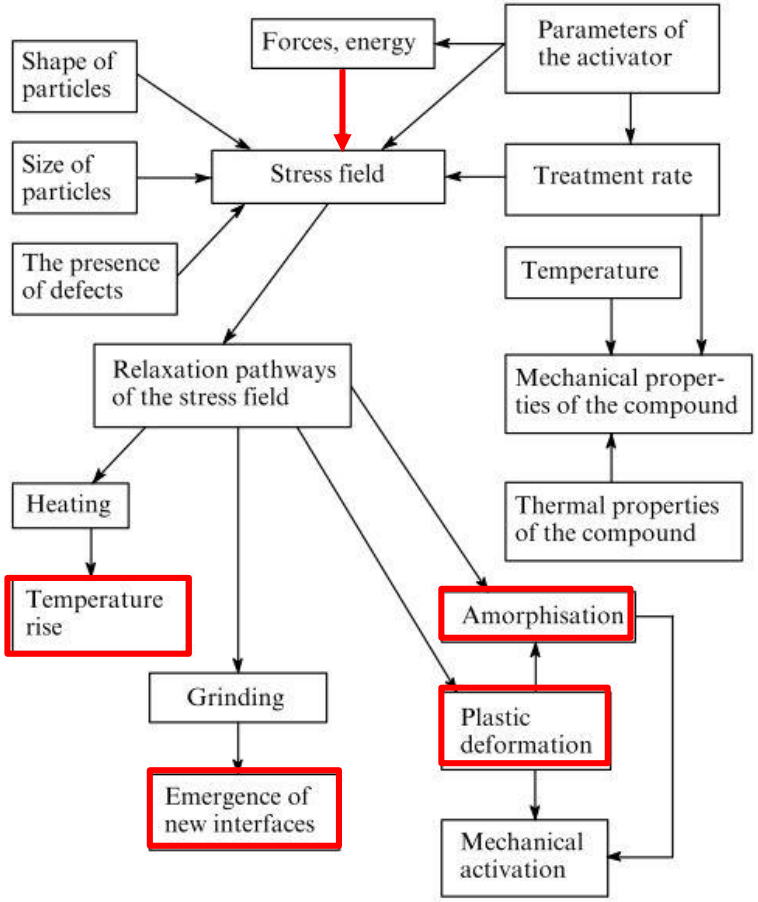
Mechanical activation of solids



⊕ Increase reaction rate

⊕ Decrease energy consumption

⊕ More environmentally friendly

⊕ Easy and simple

V. Boldyrev, Russian Chemical Reviews, 2006, 75, 177-189

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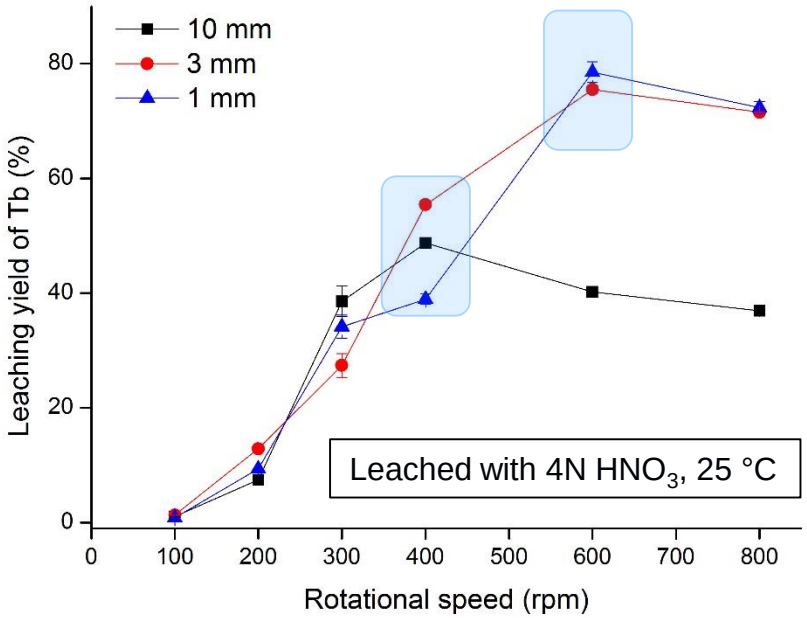
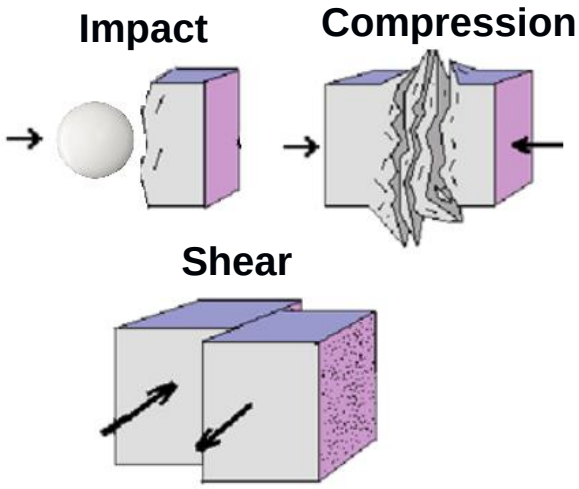
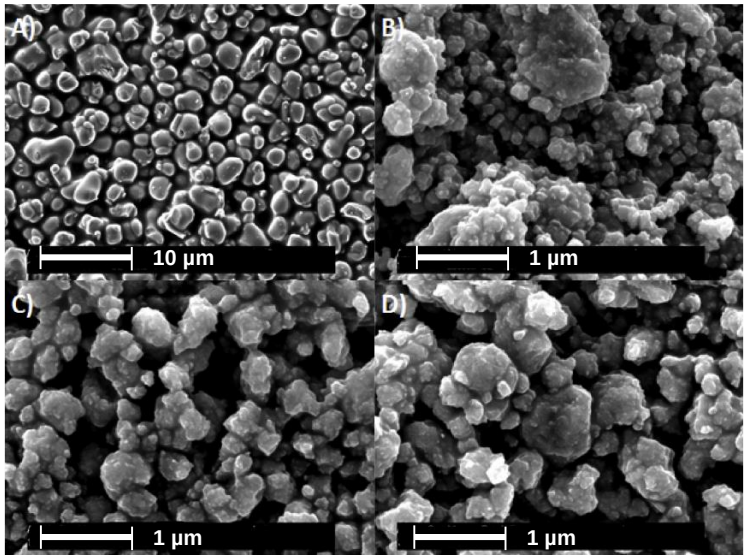
Impact force versus shear stress

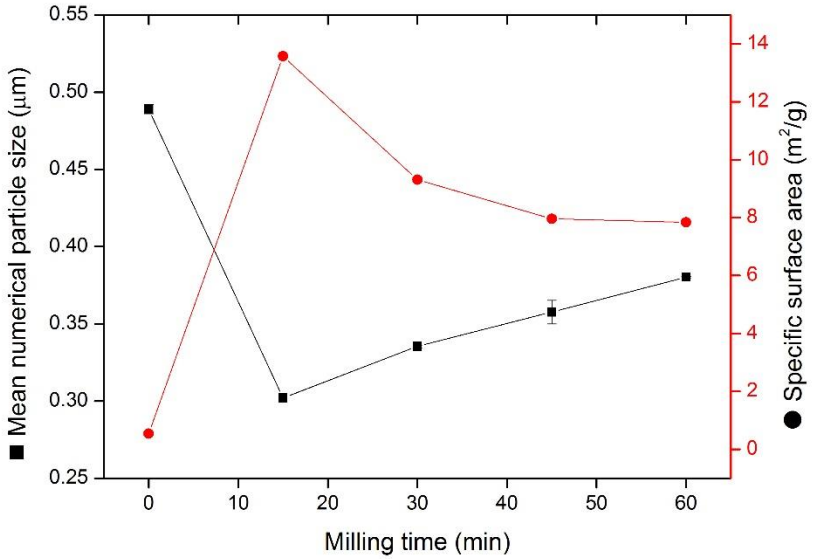




- Similar pattern in function of rotational speed
- Smaller grinding balls = beneficial
- Process is more shear-induced

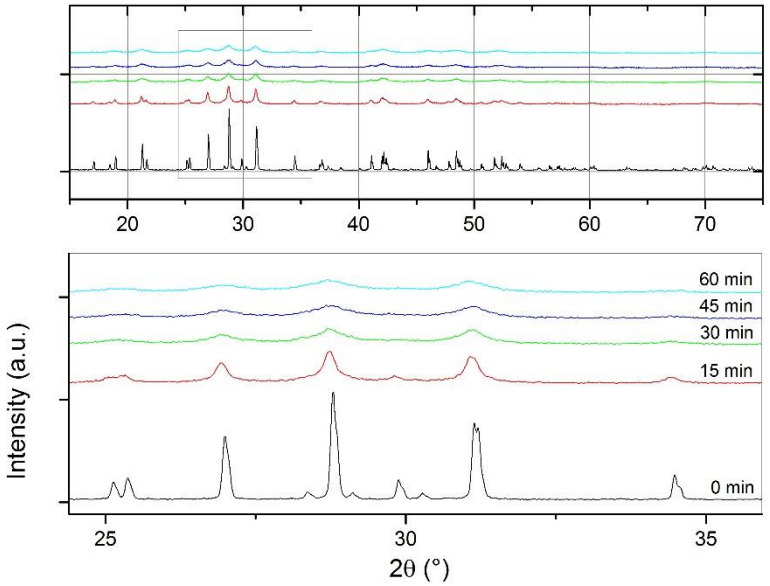
The influence on size and shape

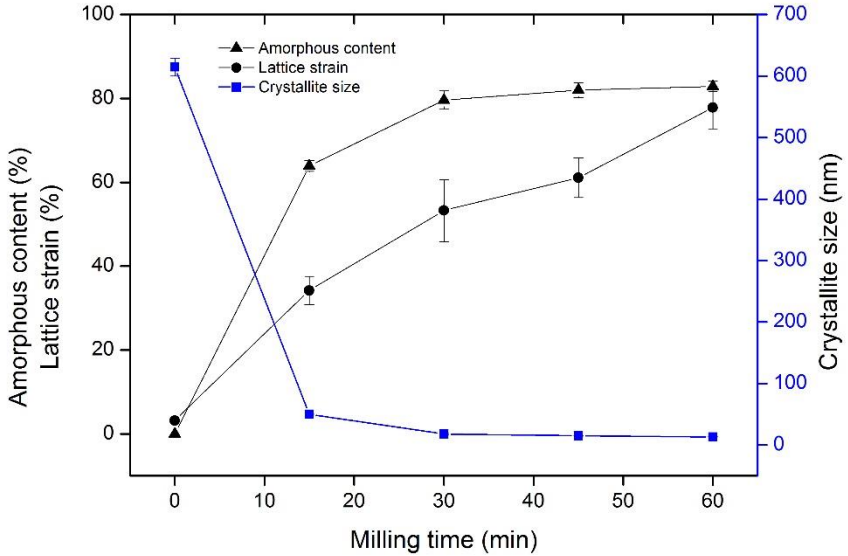




- Agglomeration due to cold welding of particles
- Increase in particle size
- Decrease in specific surface area

Structural disordering of crystal structure





- Reduced peak intensity and peak broadening
- Increasing amorphous content and lattice strain
- Decreasing crystallite size

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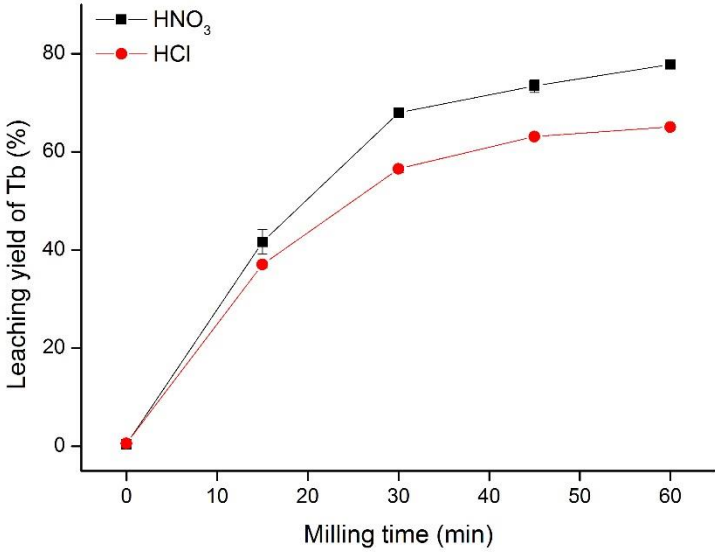
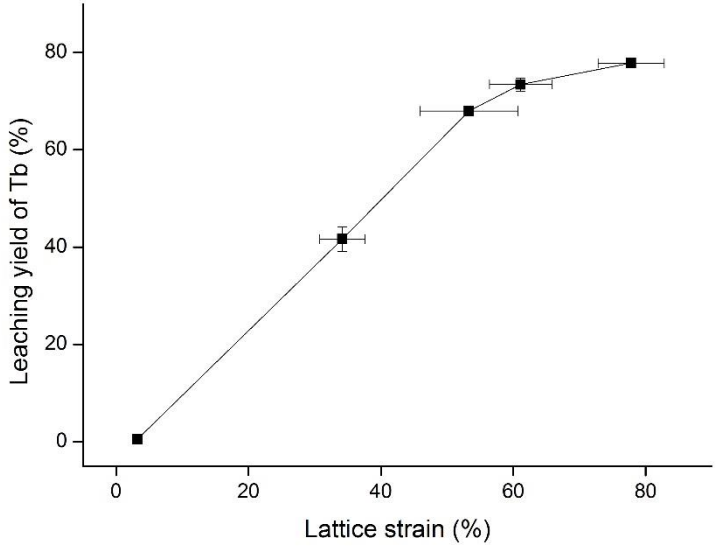
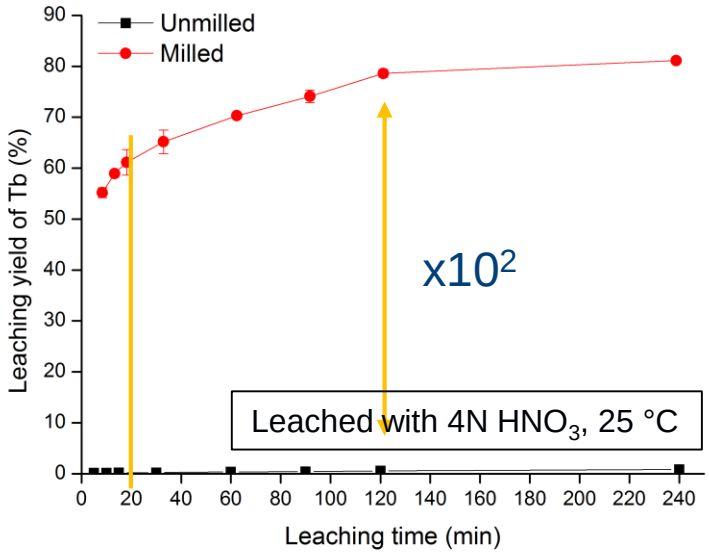
Mechanical activation mechanism

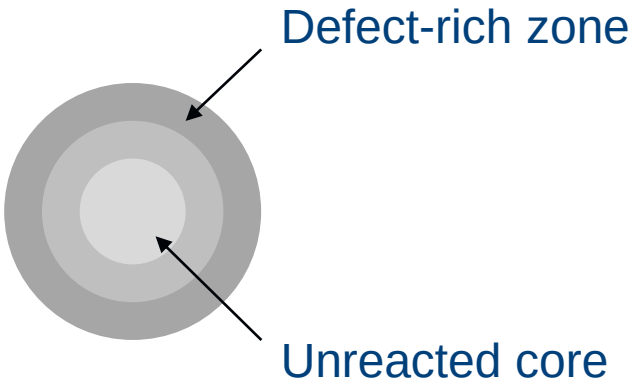




- Higher recovery rates with 4N HNO_3
- Improved leaching is determined by mechanical deformation of crystal structure
- Correlation of leaching yield and lattice strain

Mechanochemistry versus hydrometallurgy





- Substantial improvement in leaching yield
- Change in leaching pattern
- Identification of different crystal defect zones

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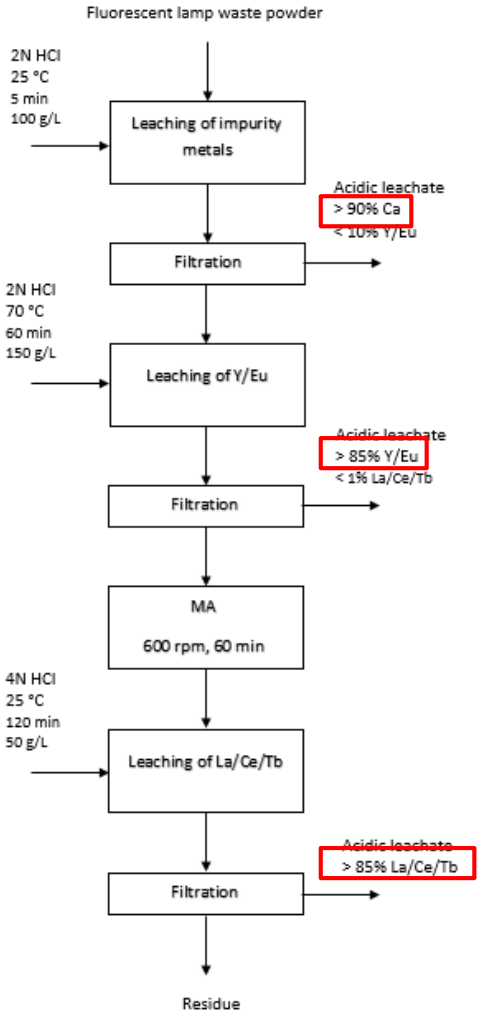
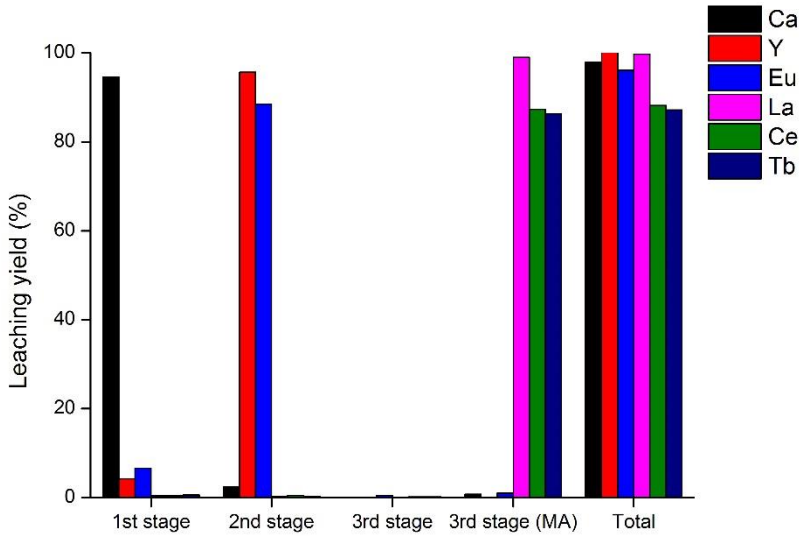
From waste to resources





- Concentrated leachates (Ca / Y and Eu / La, Ce and Tb)
- No recovery of La/Ce/Tb without MA
- Improved mechanical activation due to cullet

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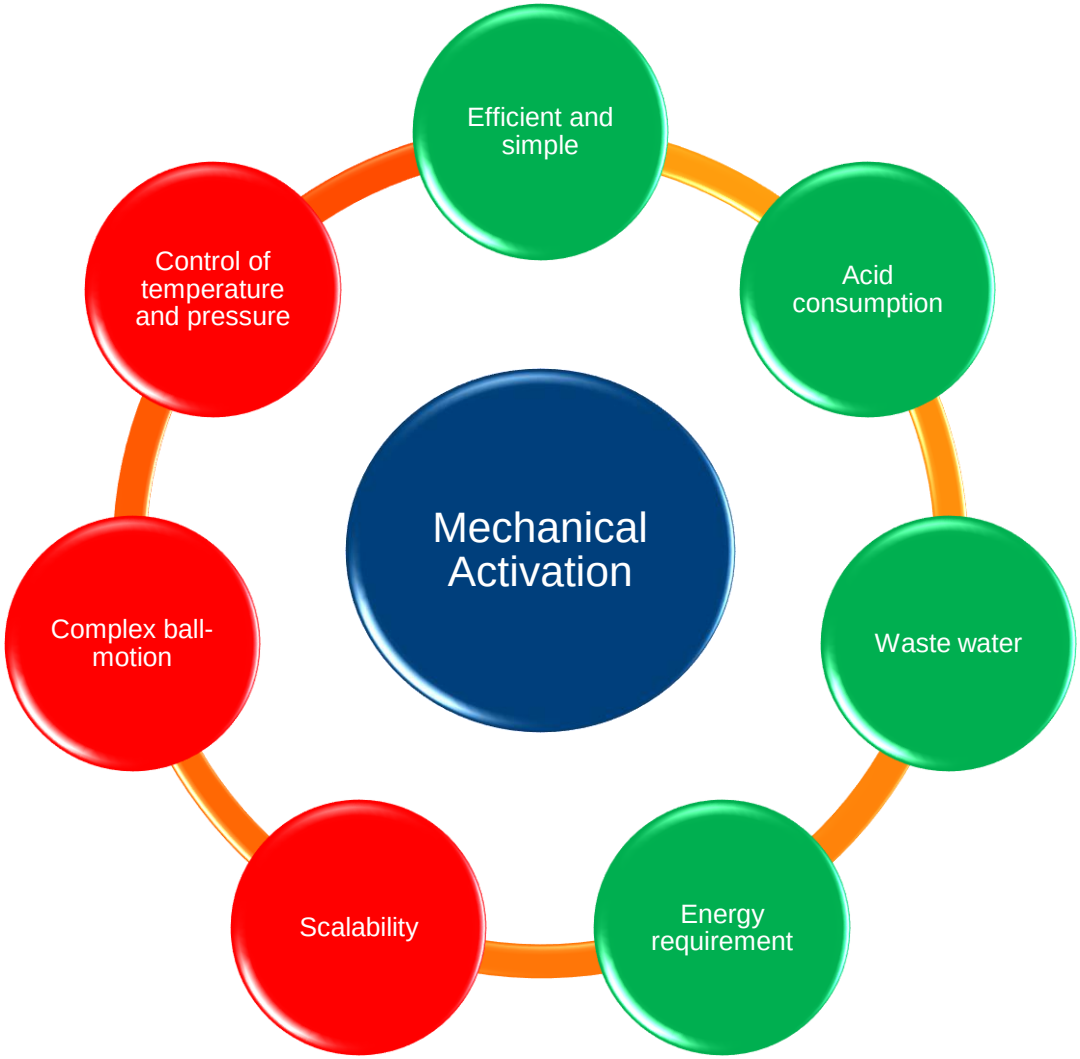
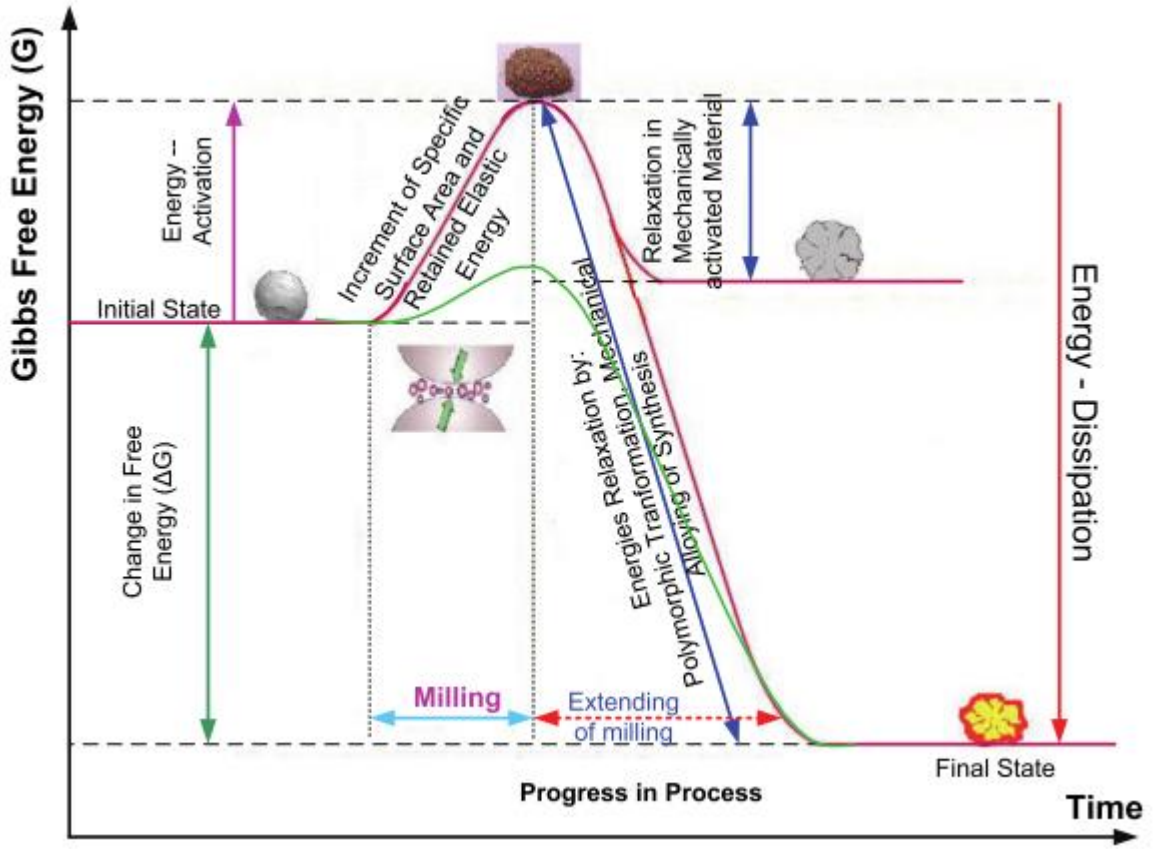

Mechanical Activation
Efficient and simple
Acid consumption
Waste water
Energy requirement
Scalability
Complex ball-motion
Control of temperature and pressure

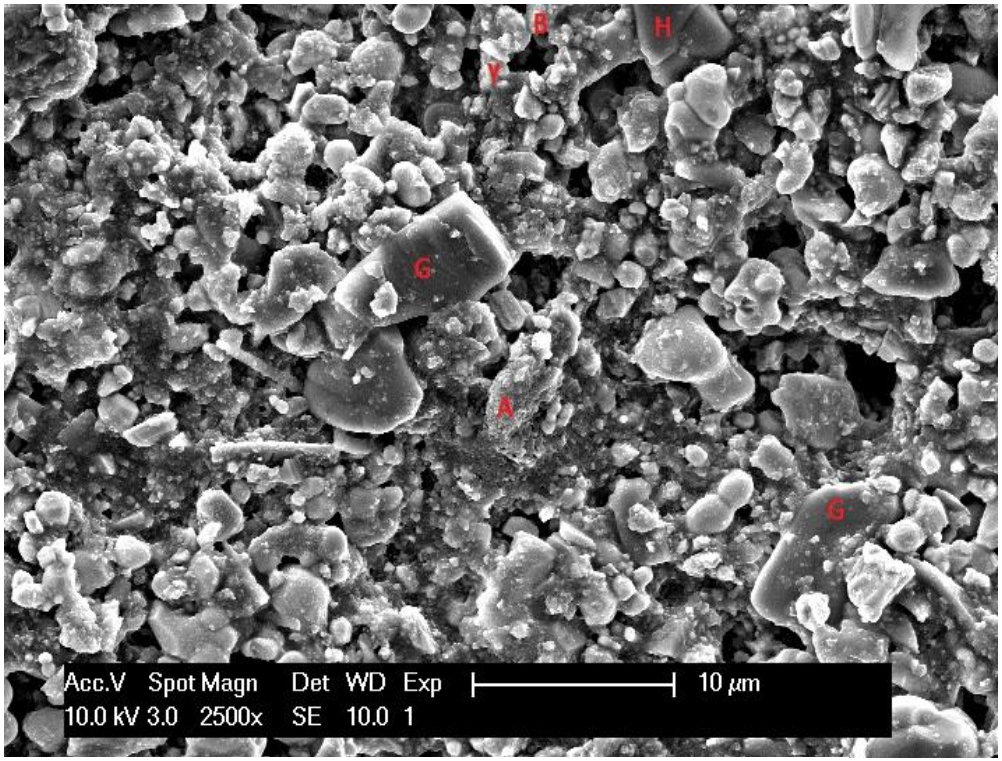
Questions?

Research funded by a Ph.D. grant of the Agency for Innovation by Science and Technology (IWT)

Mechanically activated state



Composition of lamp phosphor waste



Element	wt%	Element	wt%
Al	11.05	Mn	0.54
Ba	2.10	Na	7.14
Ca	21.42	P_x	10.64
Ce	3.05	Sb	0.36
Cl	0.50	Si	10.89
Eu	1.30	Sr	2.47
La	3.94	Tb	1.28
Mg	0.88	Y	19.62

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